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(2+1) REMPI OF NO VIA THE D $^2\Sigma^+$ STATE: ROTATIONAL BRANCHING RATIOS

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Recent photoelectron spectroscopic studies in a (2+1) REMPI of NO via the Rydberg D $^2\Sigma^+$ state have revealed anomalous ionic rotational branching ratios. We have performed ab initio calculations of these branching ratios and find that the *molecular nature* of the ionization continuum plays an essential role in the dynamics. Even though the bound orbital is very atomic-like (>98% p-like), the photoelectron continuum wavefunction is quite sensitive to the non-spherical nature of the molecular ionic potential and causes a strong persistence of the p-partial wave which, in turn, leads to a large $\Delta N=0$ peak.

High resolution studies of photoelectron spectra (PES) produced by resonant-enhanced multiphoton ionization (REMPI) of individual ro-vibronic states are an important probe of the dynamics of such photoionization processes. Whereas ionic rotational states have been resolved in the photoelectron spectrum of H_2 with relative ease [1,2], the resolution of ionic states in heavier molecules has been very difficult because of the smaller rotational constants. Such studies have only been recently performed in NO [3–5]. The (1+1) REMPI PES of NO by Wilson et al. [4] revealed a number of peaks corresponding to various values of the difference (ΔN) in the angular momentum quantum numbers for the excited state (N_i) and the ion (N_+) ($\Delta N \equiv N_+ - N_i$). Ab initio calculations [6] of ionic rotational branching ratios helped to clarify some features of these spectra such as the dominance of the $\Delta N=0$ peak and the suppression of the $\Delta N=\pm 1$ peaks. The recent (2+1) REMPI PES via the D $^2\Sigma^+$ ($3p\sigma$) state of NO by Viswanathan et al. [5] shows a strong $\Delta N=0$ peak. Due to the selection rule [6,7] $\Delta N+l=$odd, valid for ionization of a Σ state leaving the ion in a Σ state, a $\Delta N=0$ peak, of significant intensity implies that the photoelectron orbital must have substantial odd-wave (p, f, ...) character. This, combined with the "pure" Rydberg p nature of the 7σ orbital in the D state, led the authors of ref. [5] to suggest that there may be a strong *l*-mixing in the ionization continuum. In this communication, we present results of ab initio calculations of these ionic rotational spectra and compare them with the data of ref. [5]. Indeed, we find the p wave to be quite significant in the composition of the photoelectron orbital, hence accounting for the strong $\Delta N=0$ peak. More importantly, these results illustrate the need for an adequate description of electronic continuum states in quantitative studies of low-energy photoionization dynamics.

Our calculations were done using the theoretical framework described earlier [8]. The photoelectron wavefunction is calculated in the frozen-core Hartree–Fock approximation using the iterative Schwinger variational technique for an internuclear separation of 2.008 a_0. This is the equilibrium internuclear distance for the NO^+ ion and most of the

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Rydberg states of NO. We use a Gaussian basis set of (10s6p1d) on each atom contracted to [6s4p1d], supplemented with a (7s7p) uncontracted Gaussian basis at the center of mass (c.m.) of the molecule. This large and diffuse basis set on the origin assures the proper diffuseness of the Rydberg states. The electronic wavefunction of the 7σ orbital of the $D\,^2\Sigma^+$ state is calculated in the improved virtual orbital (IVO) scheme [9], using the NO^+ core ($E(NO^+) = -128.94691$ au). The total energy of the $D\,^2\Sigma^+$ state in this approximation is -129.03866 au. The use of the NO^+ core is based on the large relaxation of the NO core in the D state, compared to the ground state. Further details will be given elsewhere [10].

The 7σ IVO orbital calculated using the NO^+ core has 0.5% s, 99.2% p, and 0.1% d character, in a single center expansion about the c.m., in agreement with literature values [5,11]. For a photoelectron kinetic energy of ≈ 0.66 eV [5] the relative transition moments which are proportional to $|r_{fi}^{l\lambda\mu}|^2$, as defined by eq. (13) of ref. [6], are 0.0498 ($l=0$), 0.0566 ($l=1$), 0.0424 ($l=2$), 0.0047 ($l=3$), and 0.0002 ($l=4$) in the $k\sigma$ channel, and 0.0141 ($l=1$), 0.2093 ($l=2$), 0.0134 ($l=3$), and 0.0019 ($l=4$) in the $k\pi$ channel. These results support the conclusions of Viswanathan et al. [5], that the $l=1$ (p wave) is indeed present and very strong in the continuum. Note that an "atomic" like analysis would have predicted ionization into s and d waves only. The unusually large strength of the p wave is a consequence of the *l-mixing in the photoelectron continuum*, caused by the non-spherical potential of the molecular ion. The core potential for higher Rydberg states approaches the potential of the ion, and this is expected to cause similar anomalous features in photoionization out of higher Rydberg states.

In fig. 1 we compare the calculated photoelectron spectrum with the experimentally measured ones for two-photon resonant excitation via the S_{21} (11.5) line. This transition was chosen as it is unmixed and the calculation of relative M_J populations in the excited state is simple. Our calculated rotational branching ratios are convoluted with a Lorentzian detection function having a fwhm of about 6 meV. The agreement of the theoretical and experimental PES is quite good for detection parallel and excellent for detection perpendicular to the laser polarization.

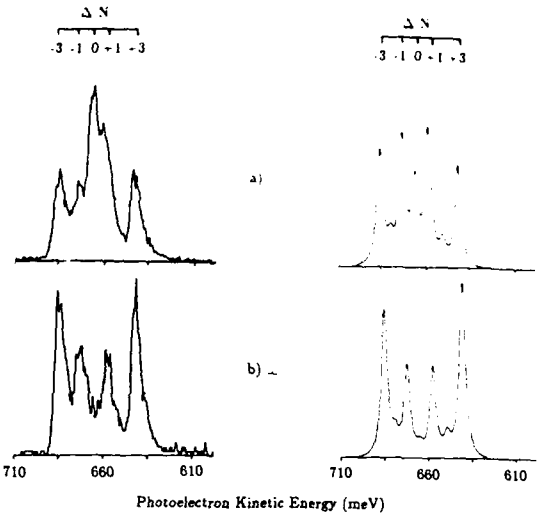

Fig. 1. Experimental [5] (left) and calculated (right) photoelectron spectra with the laser tuned to the S_{21} (11.5) line of the $X\,^2\Pi \rightarrow D\,^2\Sigma^+$ transition of NO, for (a) laser light polarized parallel ($\parallel$) to detection, (b) laser light polarized perpendicular ($\perp$) to detection.

The $\Delta N=0$ peak is quite significant in the parallel detection and is small, as observed experimentally as well, in the perpendicular detection. Combined with the selection rule $\Delta N + l = \text{odd}$, these results point to significant odd-l partial waves. More importantly, the good qualitative agreement between the theory and experiment illustrates the ability of ab initio calculations to unravel subtle features in the photoionization dynamics.

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